

AD-A016 123

PERFORMANCE EVALUATION OF A FUSED-ALKALI ELECTROLYTE,
INTERNAL-REFORMING FUEL CELL

Edward J. Taborek

Army Mobility Equipment Research and Development
Center
Fort Belvoir, Virginia

April 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

ADA016123

302159

AD

Report 2142

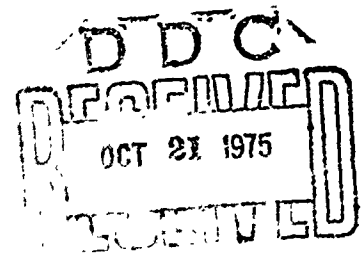
PERFORMANCE EVALUATION OF A FUSED-ALKALI
ELECTROLYTE, INTERNAL-REFORMING FUEL CELL

April 1975

Approved for public release; distribution unlimited.

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
US Department of Commerce
Springfield, VA 22151

U. S. ARMY MOBILITY EQUIPMENT RESEARCH AND DEVELOPMENT CENTER
FORT BELVOIR, VIRGINIA



A

37

3

White Section	<input checked="" type="checkbox"/>
Dark Section	<input type="checkbox"/>

A

PREFACE

The fuel cell system which was evaluated at the Electrochemical Division, Electrotechnology Department, USAMERDC, was developed by Prototech, Inc., in conjunction with Atlantic-Richfield Corporation. In addition to the references cited in the text, information on the system was obtained by personal communications between the author and employees of Prototech, Inc., and the Atlantic-Richfield Corporation.

The author hopes that in any future investigation on this system this report will serve as a guide to avoiding the pitfalls which were experienced in his work on the system.

Appendixes A and B are reproductions of information furnished by Prototech, Inc., and are not intended to represent exactly the values or conditions used in this work.

CONTENTS

Section	Title	Page
	PREFACE	iii
I	INTRODUCTION	
	1. Background	1
II	THEORY	
	2. Principles of Operation	1
III	EXPERIMENTAL EQUIPMENT AND PROCEDURES	
	3. Equipment	2
	4. Procedures	8
IV	RESULTS AND DISCUSSION	
	5. Cell Performance	10
	6. Effect of Additives	15
	7. Effect of Cathode Screen Orientation	17
	8. Difficulties and Failure Modes	17
V	CONCLUSIONS	
	9. Conclusions	19
	APPENDIXES	
	A. Liquid Hydrocarbon Feed System for Fuel Cells	21
	B. UDEX Raffinate	25

ILLUSTRATIONS

Figure	Title	Page
1	Fuel Cell Cutaway	4
2	Internal Structure of Anode	6
3	Cell Performance on Hydrogen Fuel	11
4	Cell Performance on Methane Fuel	13
5	Power from Methane Fuel	14
6	Fuel Cell Performance on UDEX Fuel	16
A-1	Liquid Hydrocarbon Feed System	22
A-2	Approximate Calibration Curves for Liquid-Feed Capillaries	23

PERFORMANCE EVALUATION OF A FUSED-ALKALI ELECTROLYTE, INTERNAL-REFORMING FUEL CELL

I. INTRODUCTION

1. **Background.** In the fall of 1968, Walter Juda described an internal-reforming fuel cell which operated at 500° C with hydrocarbon fuels and a molten alkali electrolyte.¹ This system had been developed at Prototech, Inc., and at Atlantic-Richfield Corporation; but by the time Juda's paper was presented, the two companies already had discontinued further development of the system.

After this, a decision was made at the U.S. Army Mobility Equipment Research and Development Center (USAMERDC) to further test the system to determine the extent of its capabilities and limitations with possible further development if warranted by the test results.

A complete test stand was purchased from Prototech, including cells and accessories, for operation on either liquid or gaseous fuels. When the test stand was delivered, a technician from Prototech spent 2 days checking out the system and demonstrating its operation to a USAMERDC engineer, who subsequently never worked on the project. After about 1 year, the author was assigned to carry out the testing program.

By the time testing began, the necessary techniques for successful operation of the system had been forgotten by the USAMERDC engineer who was originally assigned the project and indeed had begun to fade somewhat in the minds of those who had worked for years to develop the system to its present state.

Although it was anticipated that the test program would include evaluation of different fuels than had previously been used with the system, the major achievement of the project was the rediscovery and recording in USAMERDC's Electrochemical Division laboratory of the necessary techniques and precautions for obtaining appreciable operating lifetimes from the system.

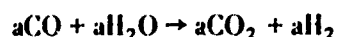
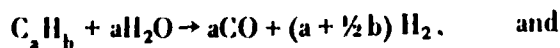
II. THEORY

2. **Principles of Operation.** In this reforming system, a hydrocarbon or mixture of hydrocarbons is used as fuel. The fuel is heated, humidified, and exposed to a

¹ W. Juda et al., Abstract No. 353 in *Extended Abstracts*, The Electrochemical Society, Inc., New York, N.Y., 134th National Meeting, 1968. (See also R. L. Novack, D. M. Moulton, and W. Juda, French Patent 1,497,014 (6 October 1967).)

reforming catalyst where the steam-reforming reaction $\text{--CH}_2\text{--} + \text{H}_2\text{O} \rightarrow \text{CO} + 2\text{H}_2$ and the water-gas shift reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ produce hydrogen, which is then utilized as the fuel for a hydrogen-oxygen fuel cell.

For a general hydrocarbon, the overall result of the steam-reforming and shift reactions may be written:



A side effect to the reforming reaction, is the methanation reaction $3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ in which the products undergo a reverse reaction.

After being liberated from the fuel, the hydrogen diffuses through a permeable palladium foil.² Upon arrival at the electrode-electrolyte interface it undergoes the oxidation half-reaction $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$.

Just as the fuel must be converted from its original hydrocarbon form, so, too, the oxygen for the cathodic reduction undergoes an initial homogeneous transformation. Upon being heated to a temperature in the neighborhood of 500° C, the electrolyte, into which air is continually fed, becomes substantially anhydrous, darkens because of the formation of superoxide ion in the reaction $4\text{OH}^- + 3\text{O}_2 \rightarrow 4\text{O}_2^- + 2\text{H}_2\text{O}$, and is consumed cathodically by the half-reaction $\text{O}_2^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow 4\text{OH}^-$.

No noble-metal catalyst is necessary for the cathodic reaction.³ Instead, it is catalyzed by nickel oxide which is formed at the surface when nickel is heated strongly in air.

III. EXPERIMENTAL EQUIPMENT AND PROCEDURES

3. Equipment.

a. **General.** The test stand (purchased from Prototech, Inc., Newton Highlands, Massachusetts) consisted of a frame assembly to which was attached the necessary flowmeters, valves, and tubing for directing, mixing, and controlling the flow of gases from compressed-gas cylinders or other sources to the fuel cell.

² W. Juda, U.S. Patent No. 3,407,094 (October 22, 1968).

³ D. Moulton et al., U.S. Patent No. 3,471,335 (October 7, 1969).

Other accessory equipment included a filter for removing carbon dioxide and water from the air, a saturator for introducing a controlled amount of water vapor into the fuel-gas stream, a constant-temperature oil bath with circulating pump for regulating the temperature of the saturator, an assembly for introducing and vaporizing liquid fuel at a controlled rate, a condenser for trapping water vapor leaving the cell with the spent fuel, and electrical cables, load resistors, and meters for measuring voltage and current. The stand was designed to accommodate two fuel cell systems operating simultaneously, but space in the laboratory where the test stand was set up was insufficient to permit operation of more than one cell at a time.

b. **Cell Assembly.** The cell assembly contained three major parts: the cathode-container assembly, the lid assembly, and the anode assembly. In addition, a reference electrode was placed in the electrolyte. The cell assembly is shown in a cutaway view in Figure 1.

(1) **Cathode-Container Assembly.** The cathode-container assembly was a flanged nickel box into which the cathode screen assemblies were welded. Each screen assembly was made of four thicknesses of nickel screen, 4 by 3-5/16 inches, which were spot welded to a piece of 9-mesh nickel screen, 4-1/8 by 4-7/16 inches, which acted as a support and current collector. Two pairs of grooves were machined into the container's interior ends to position the screen assemblies. The screen assemblies were fastened to the container by means of a strip of nickel foil, which was folded over the screen and spot welded to both the screen and the container for mechanical integrity and electrical contact. Another strip of nickel foil was welded to the outside of the case to act as a convenient connecting link from the cathode to the positive side of the external circuit.

In order to convert the surfaces of the screens and cell-body interior to the required catalytic nickel oxide, the container was heated to red heat in air until the surfaces turned black. This had to be accomplished after the screens were installed because the spot welding required shiny metal surfaces. The extended, nickel-foil strip was protected from heating as much as possible in order to keep the outer edge oxide-free for better electrical conductivity.

(2) **Lid Assembly.** The lid was a flat 1/8-inch-thick rectangle of nickel whose dimensions were those of the flange on the container. On its top were welded 10 nickel tubes. Two of these were to accommodate the inlet and outlet tubes of the anode, four were for the air-inlet tubes, one was for the thermocouple, one was for the reference electrode, one in the center was for the used-air outlet, and one—smaller in diameter than the rest— was to allow the passage of the wire attached to the anode. The tubes were about 4 inches in height, which was sufficient to prevent electrolyte from splashing out and to permit the upper ends to

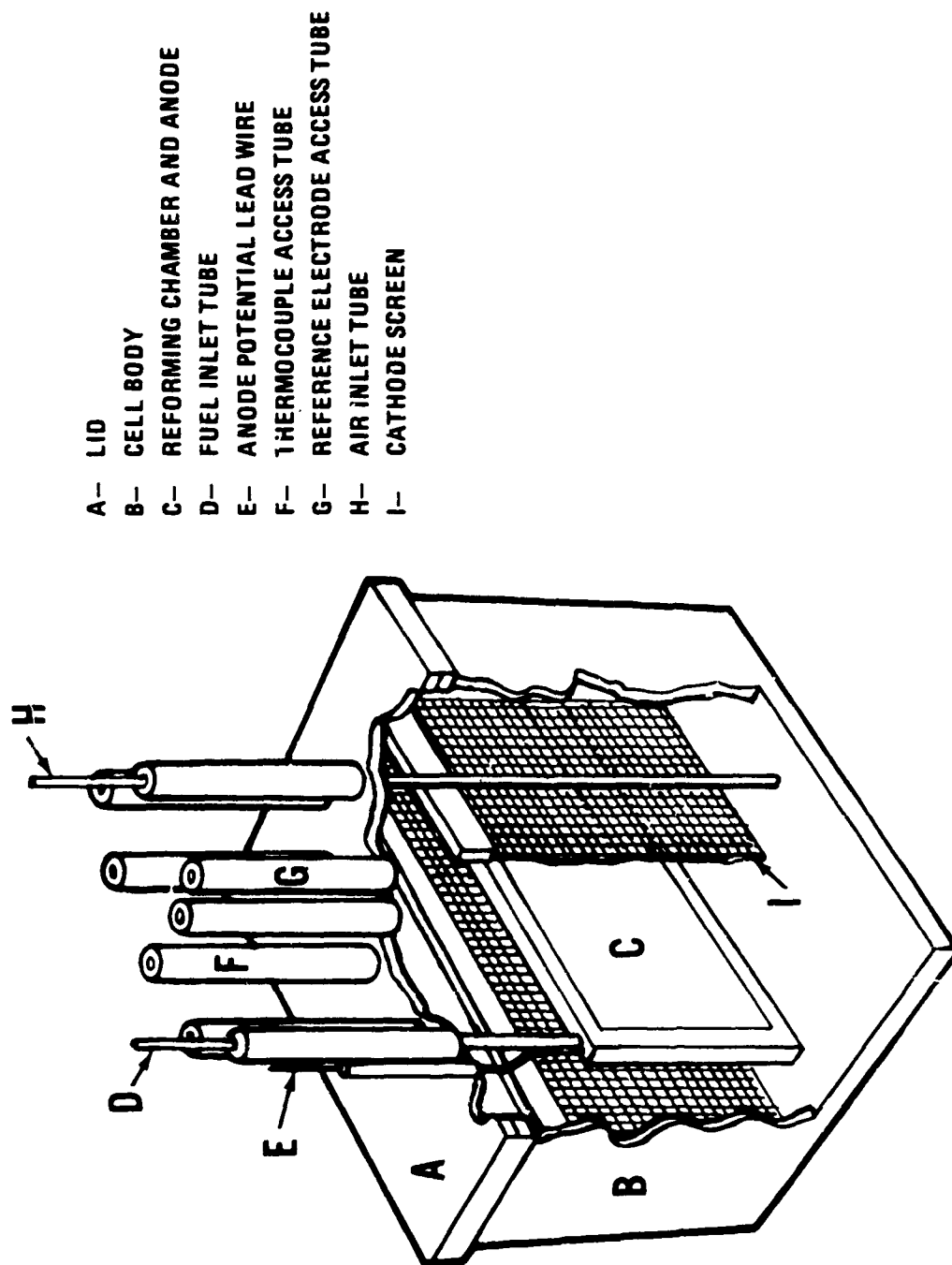


Figure 1. Fuel cell cutaway.

remain at a temperature low enough to allow Teflon insulating bushings to be placed in the top of the tubes. These bushings accommodated the anode inlet and outlet.⁴ The anode potential lead wire was insulated with ceramic fish-spine beads. The lid was secured to the flange by 12 machine screws around the periphery.

(3) **Anode Assembly.** The anode was made by welding together a nickel frame of about 2 by 4 by 3/16 inches, two pieces of palladium foil the same overall size as the frame, and two nickel covers, 1/32 inch thick. The covers were placed over the foil on the frame and heliarc welded for a leak-free seal. The nickel frame (nickel 200) was 1/4 inch wide, leaving approximately a 1½- by 3½-inch area of exposed foil on both sides with a total area of 67 cm².

The anode was filled with a deactivated Girdler G6ORS catalyst. An excessively active catalyst reportedly causes coking of the fuel and, thus, clogging of the passages with carbon.⁵ An aqueous sodium hydroxide solution was the deactivating agent. The anodes supplied by Prototech already were filled with the treated catalyst and were used as received.

Two 1/8-inch o.d. nickel tubes were soldered in with Permabraz 130. The inlet tube extended into the anode chamber for an even distribution of fuel as shown in Figure 2. The filling hole was, of course, welded closed after use.

In order to permit measurement of the IR-free anode potential, a nickel wire long enough to extend out of the cell was welded to one end of the frame of the anode assembly.

(4) **Reference Electrode.** A reference electrode, which was simply a nickel wire with an oxide coating, was immersed in the agitated portion of the electrolyte. Use of this reference wire made separate anode and cathode voltage measurements possible. Because of the position of the reference wire on the opposite side of the cathode screen from the anode, it could be assumed that the measured cathode voltage with respect to the reference was IR-free, so that the measured cathode-to-reference voltage was a fair approximation of the cathode polarization. However, because of the narrow space into which the reference wire was inserted, the author cannot express certainty that some part of the reference wire was never touching some point on the screen or container wall. For this reason, the cathode-anode voltage, rather than the electrode-reference potential, usually was measured.

⁴ R. Allen and R. Novack, U.S. Patent No. 3,640,773 (February 8, 1972).

⁵ H. G. Petrow, Prototech, Inc., private communication.

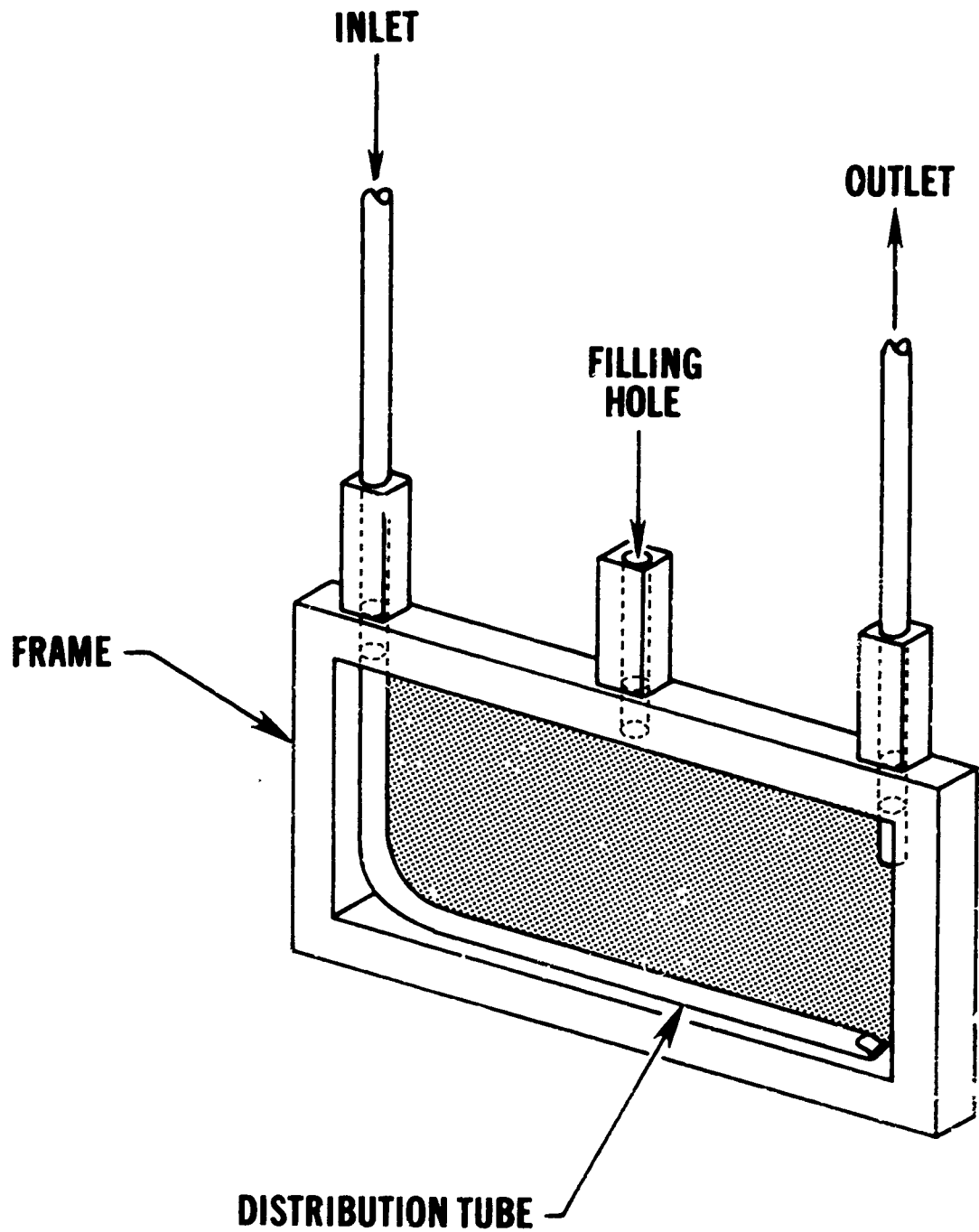


Figure 2. Internal structure of anode.

c. **Cell-Heating System.** The oven was a sheet-steel box with nichrome electrical heating wire insulated with ceramic tubes and fish-spine beads wrapped around its four sides. The turns were spaced more closely near the top of the box, where the heat loss was greatest. The splice between the nichrome wire and copper extension was covered with ceramic cement to minimize oxidation since heating occurred at the points of contact. The sheet-steel box outfitted with the heating element was inserted into a larger box, and the space between was filled with insulating material.

d. **Procedure for Assembly.** The anode tubes were inserted into the corresponding tubes of the lid until they protruded from the top end of the lid tubes. The Teflon bushings were then fitted over the anode tubes and into the tops of the lid tubes. The anode was then inserted into the container, and the lid and bushings were adjusted so that the anode cleared the bottom of the container when the lid was seated on the flange of the container. Two copper bars, which provide the connection to the negative side of the external circuit, were then clamped over the anode tubes a short distance above the top of the lid tubes. The clamping was accomplished with machine screws passing through the two copper bars. After this, the anode tubes were wrapped with wet asbestos paper for electrical and thermal insulation. When the paper had dried, nichrome heating wire was wound over the asbestos paper so that the tubes could be heated to avoid condensation of fuel or water vapor and to minimize cooling of the cell by the incoming gases. Since the anode inlet and outlet tubes are somewhat flexible, it was necessary to put the anode and lid assembly into position on the cell and then, using an ohmmeter, to adjust the anode position so that it was, as nearly as possible, centered in the cell between the screens. In this way, the probability of short circuits during operation was lessened.

A thin aluminum gasket was positioned between the lid and the cathode-container assembly to form a seal which was supposed to eliminate leakage of electrolyte between the lid and container.⁶

During the investigation, it was found that several a.c. volts appeared on the cell from the heating wire. This potential was reduced to a fraction of a volt by adding a partial layer of asbestos paper between the cell and the heating oven; however, this action reduced the thermal coupling so that the thermal stability decreased somewhat. Grounding the cell eliminated the remainder of the a.c. voltage.

e. **Fuel-Feed System.** The experimental apparatus was designed to allow a choice of either gaseous or liquid fuel. A saturator was provided in the gaseous fuel line for injection of the proper proportion of water into the fuel. When a gaseous hydrocarbon fuel was used, the fuel itself was passed through the saturator, which was

⁶ R. Novack, U.S. Patent No. 3,514,333 (May 26, 1970).

maintained at the proper temperature for the desired water-to-carbon ratio. When liquid fuel was used, nitrogen was passed through the water vaporizer. Prototech provided with the system an instruction set entitled *Liquid Hydrocarbon Feed System for Fuel Cells*, which is reproduced in Appendix A.

Although the instructions in Appendix A call for an 80:20 glycerine-water ratio, we were informed that Prototech had used a 50:50 ratio; thus, a 50:50 (v/v) mixture was used in this work. Either cobalt chloride (pink) or copper sulfate (blue) was used to color the solution for better visibility of the phase boundary between the mixture and the liquid hydrocarbon fuel. In use, the mixture required pressures generally in the range of 100 to 200 millimeters Hg to produce the desired feed rates. Because of the difference in density between the mixture and the fuel, slight, periodic increases in pressure were necessary in order to maintain a constant fuel-feed rate. Data on the UDEX raffinate, which was used as the liquid fuel because of its low sulfur content, were provided by Prototech with the system and are reproduced in Appendix B.

Flow rates of all gases were measured with calibrated rotameters.

f. **Electrolyte.** The electrolyte was a mixture of 95 percent KOH, mixed with 5 percent NaOH to lower the melting point.⁷ Weights were figured on a dry basis. The amount of mixture required to fill the cell to within 1½ inches of the top, as specified by Prototech, was 420 grams.

An additive consisting of a mixture of transition-metal oxides in a proportion of 5:5:1 by weight of C_2O_3 , Fe_2O_3 , and MnO_2 , respectively, was found by Prototech to result in a higher maximum current density when added to the electrolyte.⁸

g. **Electrical Circuit.** The external circuit of the cell consisted of adjustable resistors in series with a 50-millivolt, 50-ampere shunt from which the current was measured. Cell voltage was measured between the cell body and the wire connected to the anode. In this way, resistances in the inlet and outlet tubes and in connections to the copper bars were eliminated as sources of voltage drop.

4. **Procedures.** The following describes the final optimized procedure. Most of the data were obtained before this procedure was fully developed.

a. **Startup.** The following procedure was used to start fuel cell activity:

⁷ This ratio was recommended by H. G. Petrow, Prototech, Inc. (Private Communication).

⁸ R. Allen et al., U.S. Patent No. 3,471,332 (October 7, 1969).

(1) Heat electrolyte mixture in a 1000-milliliter nickel beaker to 500° C for a minimum of 4 hours or until the mixture acquires a straw-yellow color.

(2) Check for short circuits by assembling the cell without electrolyte. Align the anode to insure that it is centrally positioned between the two cathode screens.

(3) Place the cell assembly in the cell oven and heat to 500° C. Start heating the fuel-feed lines.

(4) Weigh out a 100-milligram portion of the additives.

(5) Remove the lid-and-anode assembly. Connect a piece of flexible tubing between the fuel-feed line and the anode inlet line. Start a flow of about 200 cm³/min of dry nitrogen through the anode.

(6) Pour the hot electrolyte into the cell. Sprinkle the additives over the electrolyte.

(7) Place the aluminum gasket on the cell container.⁹

(8) Replace the anode assembly in the cell. Note the time. Hook up power to the heating wire on the gas inlet and outlet tubes. Put the air-inlet tubes, thermocouple, and reference electrode in place. Begin sealing the lid to the cell container.

(9) About a minute after immersing the anode in the electrolyte (this time is allowed for the anode to come to the temperature of the cell), add a minimum of about 70 cm³/min of hydrogen to the gas stream through the anode. Start an airflow of 300 cm³/min through the air-inlet tubes.

b. **Operation.** The fuel cell should be operated as follows:

(1) Once the cell has been started, place a load upon it. The normal operating condition is for maximum power to be obtained, which is at an operating voltage of 0.60 to 0.65 volt.

(2) When desired, a different load, fuel rate, air rate, etc. can be used. After the desired changes have been made, steady state operation (constancy of

⁹ Prototech recommended presoaking the gasket in the hot electrolyte for 1 or 2 minutes before assembly (H. G. Petrow, private communication).

voltage and current) should be obtained before recording the results; otherwise, a transient, which may not be reproducible, is being recorded.

(3) According to information from Prototech, useful $\text{H}_2\text{O}:\text{C}$ ratios are 2.3 to 2.4:1 for methane fuel and 2.8 to 2.9:1 for propane. For methane, this requires a saturator temperature of 90.4°C and for propane, a saturator temperature of 96.9°C .

c. **Shutdown.** The following procedure is used for shutting off the fuel cell:

(1) Reduce the fuel rate and the air rate to minimum values, as described in the startup procedure.

(2) Loosen the screws holding the lid to the cell container.

(3) Shut off the fuel, and purge the anode of fuel with nitrogen. This should continue for 3 or 4 minutes. In the meantime, the power to inlet and outlet tube heaters may be disconnected, the air-inlet tubes may be removed, the cables may be disconnected, and the lid-fastening screws may be removed.

(4) Disconnect the anode inlet tube from the fuel feed system and remove the lid-and-anode assembly from the melt.

(5) Remove the thermocouple and shut off the power to the cell-heating oven.

IV. RESULTS AND DISCUSSION

5. Cell Performance.

a. **Hydrogen Fuel.** A few tests were performed with hydrogen to eliminate the internal reformer as a variable in evaluation of the cell. The results obtained are shown in Figure 3. The four lines represent H_2 flow rates of 60, 90, 120, and $420\text{ cm}^3/\text{min}$, corresponding to theoretical currents of 8, 12, 16, and 56 amperes, respectively. The data were very scattered; results obtained on different runs were often quite different. The lines on the graph represent a rough estimate of the average performance. These indicate good efficiency of 67 to 87 percent at an operating voltage of 0.6 volt and H_2 feed rates of 60 to $120\text{ cm}^3/\text{min}$; but at $420\text{ cm}^3/\text{min}$, the current efficiency was only about 34 percent at 0.6 volt.

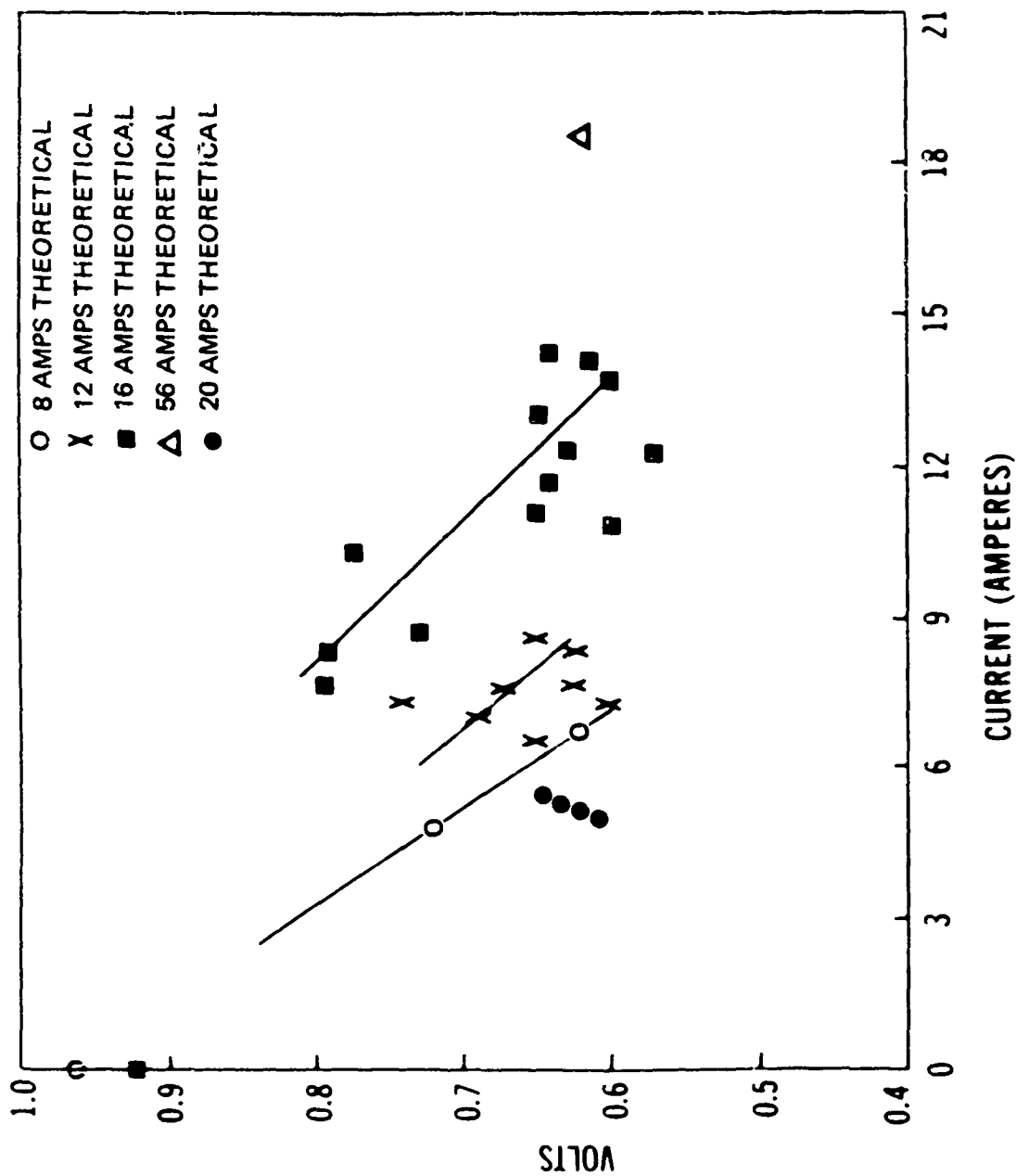


Figure 3. Cell performance on hydrogen fuel.

b. **Methane Fuel.** Current-voltage curves for four combinations of fuel- and air-feed rates are shown in Figure 4. The slopes of the straight-line portions of the current-voltage curves were interpreted as resulting from a linear relationship between fuel-flow rate, airflow rate, and cell resistance. Calculation by the method of least squares yielded the equation:

$$R = 0.0133 - 5 \times 10^{-5} M + 3 \times 10^{-5} A,$$

where R is the slope of the straight portion of the polarization curves, M is the methane-feed rate in theoretical amperes, and A is the air-feed rate in cm^3/min .

On the lower end of the voltage scale, it can be noted that curves 1 and 4 incline downward more steeply than do curves 2 and 3. Since curves 1 and 4 represent the current-voltage behavior at the lowest airflow rate, it may be inferred that their steep drop was caused by insufficient oxygen supply at the highest currents. Fuel limitation must also contribute to the drop in curves 1, 2, and 3 since curve 4 at the higher fuel-feed rate had a higher limiting current than any of the others.

Unfortunately, gathering of data was curtailed when the supply of anodes was exhausted so that additional fuel- and air-rate levels and other variables could not be investigated. However, if relationships between current, voltage, and air-feed rate as shown in curves 1, 2, and 3 apply also to the 80-theoretical-ampere methane-feed rate, then an increase in air-feed rate to 850 or 1,060 cm^3/min would have resulted in increases of, perhaps, only 1 to 2 amperes at 0.6 volt and 3 to 4 amperes at 0.5 volt.

The voltage-power relation for the same data is shown in Figure 5. At the lower methane-feed rate, the 850 cm^3/min air-feed rate yielded a slightly higher maximum power than did the other two air-feed rates. Increasing the fuel rate by a factor of four resulted in a power increase of only about 20 percent at the maximum.

When the results obtained here are compared with those reported by Juda et al. at the 20-theoretical-ampere methane-feed rate, the currents observed here were only about two-thirds as much; at the 80-theoretical-ampere rate, the currents obtained were less than one-half as much as would have been expected by comparison with Juda's data.

Inspection of the data shows that the principal factor responsible for the difference is a cell resistance about 50-percent higher in the cells used in this laboratory. This causes the straight-line portions of the polarization curves from our data to have a much more negative slope than those shown by Juda et al. and also causes the current to be limited by IR drop rather than by polarization of the electrodes.

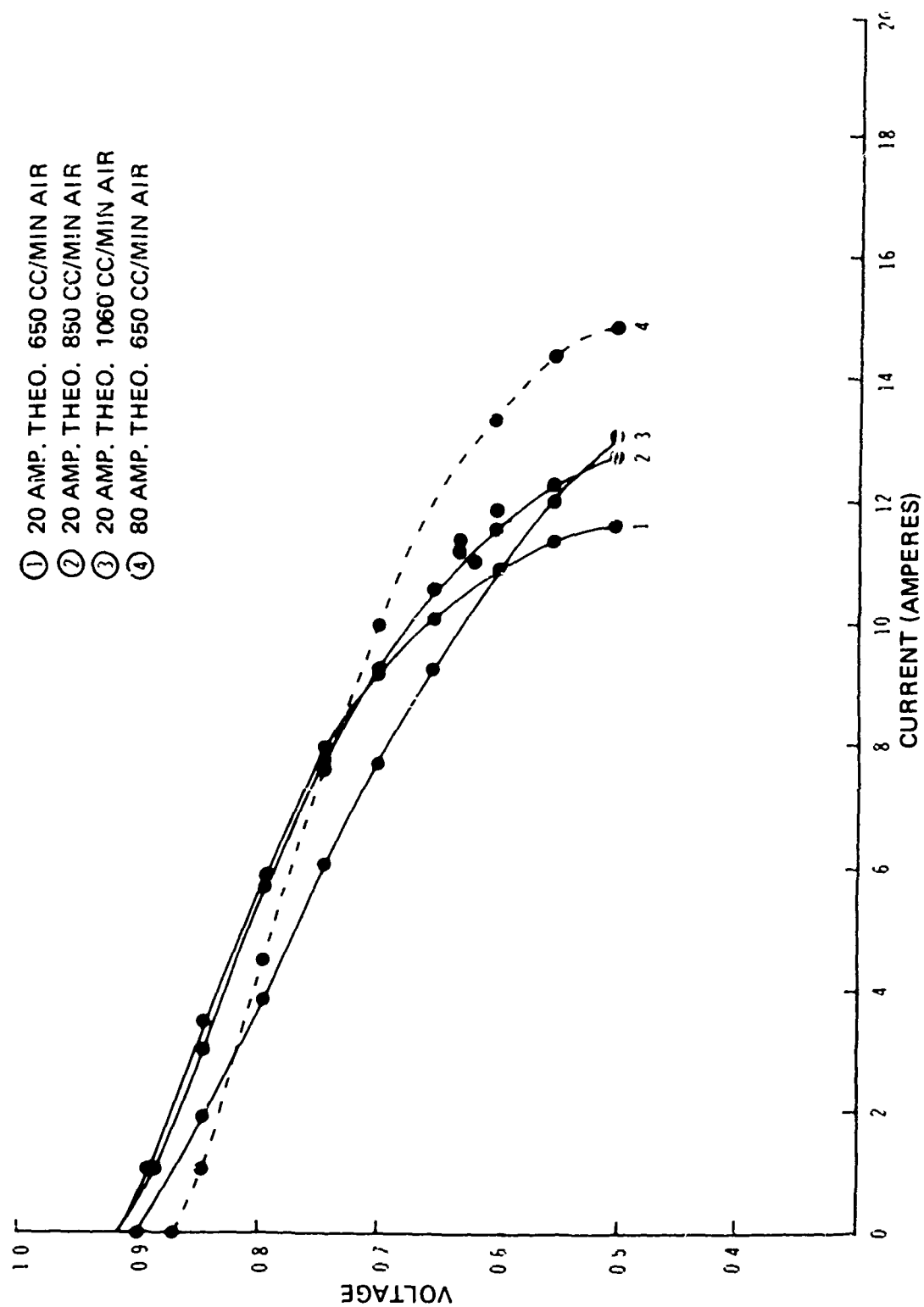


Figure 4. Cell performance on methane fuel.

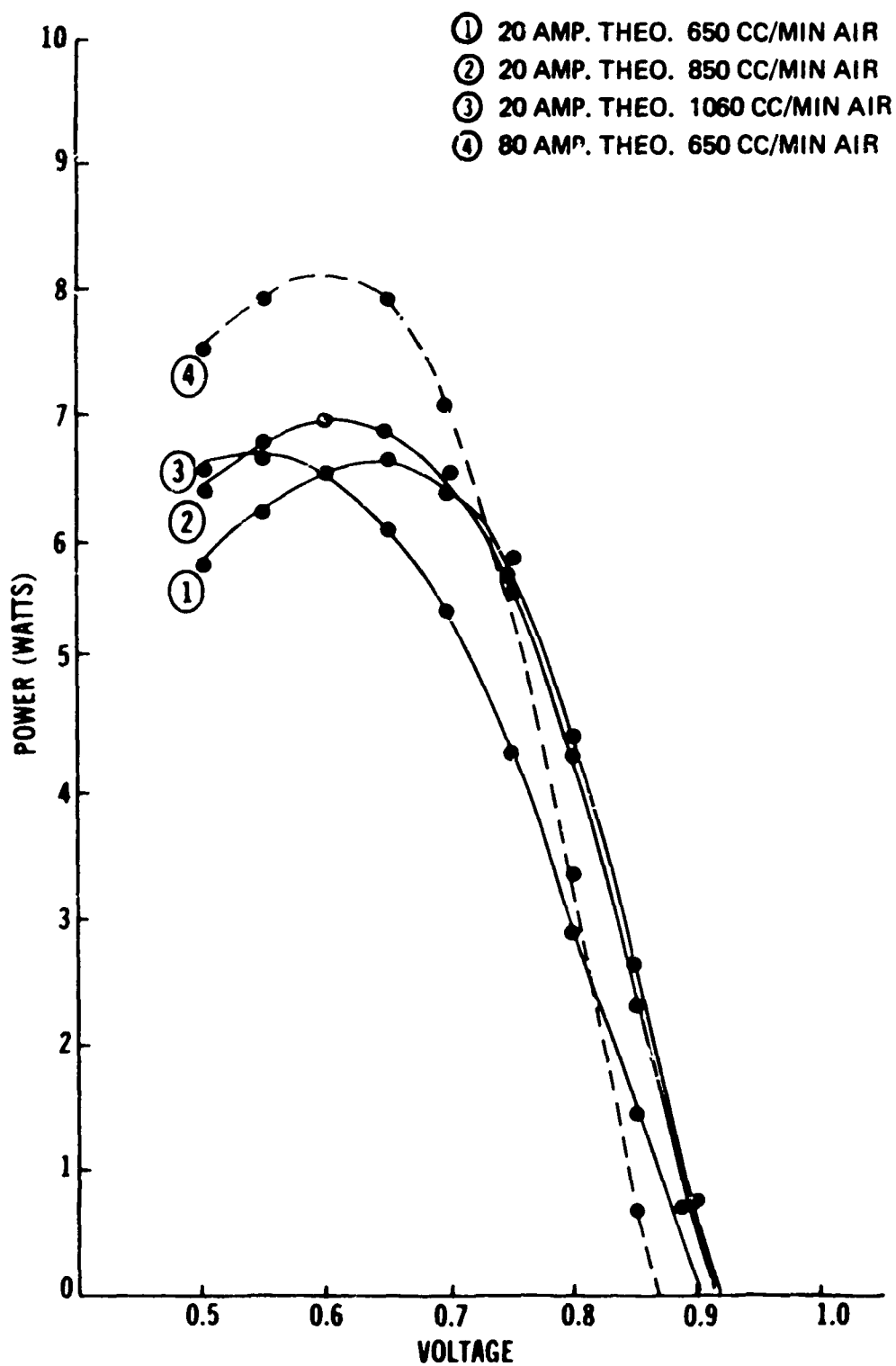


Figure 5. Power from methane fuel.

c. **UDEX Raffinate Fuel.** The results of experiments using UDEX raffinate fuel are given in Figure 6. The two lines drawn through the UDEX feed rates of 0.022 and 0.045 ml/min represent theoretical currents of about 11 and 22 amperes, respectively. The number associated with each point indicates the UDEX-feed rate in ml/min. Here, as with the hydrogen data, the data were accumulated over several runs and scatter in the data is evident. At the 0.6-volt operating voltage, the coulombic efficiency, based on the theoretical yield of hydrogen from the liquid fuel, was about 65 percent for the 0.022-ml/min feed rate and about 53 percent for the 0.045-ml/min feed rate.

d. **Relative Performance of Fuels.** Both methane and UDEX appear to operate at similar efficiencies for fuel-feed rates of about 20 theoretical amperes and below, while hydrogen delivers a somewhat higher current efficiency under favorable conditions. Because of severe scatter in the data, this effect may not be statistically significant.

6. **Effect of Additives.** In order to estimate the effect of the transition-metal oxide additives to the electrolyte, several runs were initiated without the additives. After the cell was in operation, 50-milligram portions of the additives were introduced into the cell through the available holes in the lid. In those cases where increases in current and voltage were noted following introduction of the additives, the first 50 milligrams produced the greatest increase; an additional 50 milligrams produced a barely noticeable increase again, while further additions had no effect. The table below shows the results.

Effect of Two 50-mg Doses of Oxide Additives

Run	Before Additive		After Additive	
	V (Volts)	I (Amperes)	V (Volts)	I (Amperes)
A	0.47	8.0	0.58	10.0
B	0.63	5.0	0.64	5.0
C	0.82	7.5	0.81	7.4
D	0.70	7.7	0.66	7.6
E	0.63	5.0	0.72	5.5
F	0.77	5.1	0.76	5.0
G	0.59	7.6	0.63	8.0

The degree of improvement was somewhat unpredictable, and in some cases there was actually a slight decrease in the performance. A degree of consistency is obtained, however, when the results are viewed in terms of the initial cell voltage. Those cases where the operating voltage was 0.70 volt and up responded uniformly and negatively to the addition, while those cases where the operating voltage was 0.63 volt and below all responded positively (though in varying degrees) to the addition.

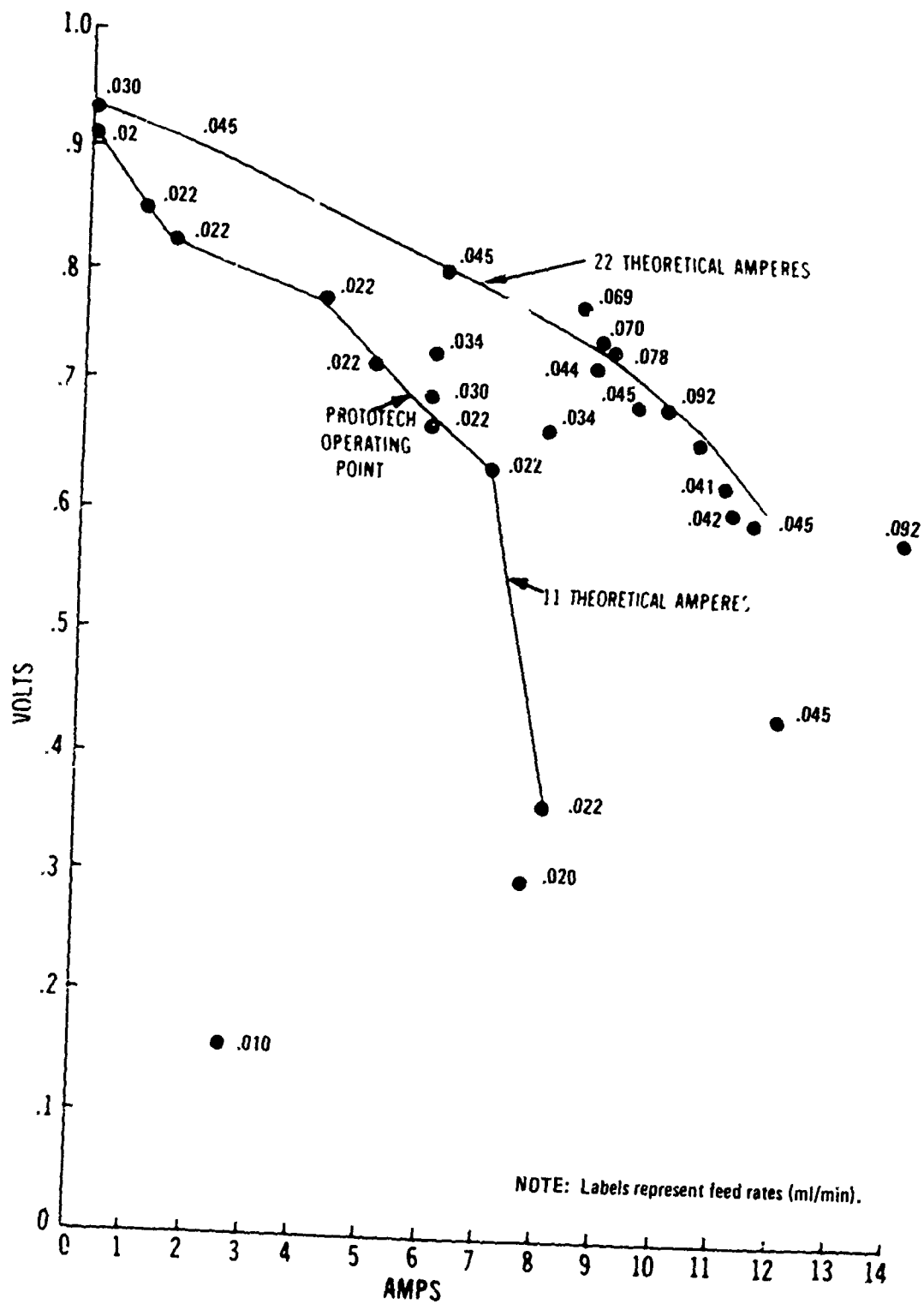


Figure 6. Fuel cell performance on UDEX fuel.

These results tend to confirm the claims made by Prototech that the transition-metal oxides increase the rate at which superoxide is produced or utilized.¹⁰ At the higher voltages, superoxide is being produced at an adequate rate to support the reaction; at the lower voltages, production or utilization of superoxide in the melt is limiting the current and power until the additive catalyst is introduced.

7. Effect of Cathode Screen Orientation. The nickel being deposited on the membranes under conditions of excess hydrogen on the membrane surface was being obtained from the cathode screens as evidenced by visible corrosion of these screens after runs in which nickel deposition was pronounced. When the original screens became badly corroded (primarily in the area of the upper edge of the electrolyte), they were replaced with new ones. Two orientations were tried: with the fine mesh screen facing toward the anode and, facing away from the anode. No difference in results could be discerned as a result of the difference in the screen's orientation, except that with the fine mesh screen toward the anode, the anode-to-cathode spacing was less, and shorting occurred more readily.

8. Difficulties and Failure Modes. The failure modes described below were experienced in a series of aborted experiments after each of which Prototech was consulted and additional information obtained.

The succeeding sections will provide guidance to any future workers on this system of the several pitfalls which must be avoided or overcome for prolonged, successful operation to be achieved.

a. Sealing. The electrolyte has a pronounced tendency to creep. The aluminum gaskets used for seals did not work satisfactorily; in every run, the electrolyte leaked out of the cell around the gasket. Prototech advised pretreating the gasket in the electrolyte for a few minutes before sealing the cell. The effectiveness of this procedure was not confirmed in this laboratory; it seemed to be immaterial whether this procedure was followed or not. Prototech explained in their patent that the efficiency of this sealing method depended on a sufficiently high temperature to soften the gasket. It might be possible that the temperature of the cell lid during operation in this laboratory was slightly low for the necessary softening to take place.

b. Corrosion. In order to prevent direct attack of the electrolyte upon the palladium foils, the presence of hydrogen is necessary. The hydrogen maintains the palladium foil at a potential which saves the palladium from corrosive attack by the electrolyte. It is not advisable, however, to maintain hydrogen continuously while warming the anode to operating temperature or cooling it back to room temperature,

¹⁰ R. Allen et al., U.S. Patent No. 3,471,332 (October 7, 1969).

because sudden and catastrophic failure accompanies a phase change at about 360° C if the foil contains hydrogen while passing through this temperature. These contradictory conditions govern the complicated startup and shutdown procedure and necessitate exposure of the unprotected foil to the corrosive electrolyte during startup and shutdown. Experience in this laboratory indicates a maximum of about three startups and shutdowns before pinhole leaks develop in the foil.

The presence of too much water in the electrolyte, in addition to preventing formation of the superoxide, is said to greatly increase the corrosion of the membrane by the electrolyte.¹¹

c. **Coking.** An overactive reforming catalyst can liberate the hydrogen from hydrocarbon and leave the carbon behind as a solid residue. This is the reason for the deactivation treatment of the catalyst with sodium hydroxide solution.

Another condition under which coking will occur is a too low H₂O:C ratio in the fuel mixture. For this reason, it is essential to maintain a continuous and adequate injection of water into the fuel.

If coking does occur to a limited extent (i.e., not completely blocking the gas flow), it can be remedied by passing an increased amount of water through the anode, accompanied preferably by an increase in temperature during this operation to increase the reaction rate of the solid carbon.

d. **Shorting.** Nickel deposition on the anode eventually will result in an internal short circuit between the anode and the cathode. The first symptom of this is "spiking" (i.e., a sudden, momentary drop in current through the external circuit). According to Prototech, this can be remedied to a certain extent by shutting off the fuel for a minute or two; this enables some of the deposited nickel to redissolve. Care is required, however, and some risk is unavoidable since the palladium membrane, then, also becomes subject to attack.

e. **Summary of Failure Modes of the Anode.** The following summarizes the failure modes described above:

(1) **Shorting**

- (a) Misalignment of anode
- (b) Dendrite formation (too high H₂ concentration on the electrolyte side of the anode)

¹¹ H. G. Petrow, Prototech, Inc., Private Communication.

(2) Corrosion

- (a) Too little fuel
- (b) Too much work in electrolyte
- (c) Too much carbonate in electrolyte
- (d) Too high temperature

(3) Blockage — Too little water in fuel

(4) Cracking — Change of temperature with hydrogen present

- (a) Cell-oven failure
- (b) Inserting or removing anode with fuel on
- (c) Too fast fuel rate through anode or insufficient preheating

V. CONCLUSIONS

9. **Conclusions.** The power output from the fuel cells used in these tests never approached the level of 400 to 500 A/ft² at 0.6 to 0.7 volt, which was expected from the claims of Prototech.¹² The maximum performance on hydrocarbon fuel was about 200 A/ft² in these tests. The power output which Prototech had stated to be 18 to 20 watts was limited to under 8.3 watts in our tests.

Open circuit voltage was never more than 0.95 to 0.96 volt as against 1.0 volt found by Prototech.

It appears that the major factor differentiating the results of this author from those of Prototech is the cell resistance. The higher cell resistance found here caused IR drop to be greater than anode or cathode polarization whenever fuel-feed rates above 20 amperes were used.

The reason or reasons for the higher IR drop in these experiments, other than a very slight difference in cell temperature, could not be identified. However, the operational difficulties encountered in conducting these tests would prohibit the use of this type of cell for all but a very limited type of application. The necessity of complicated startup and shutdown procedures involving the need to plunge the anode directly into the molten electrolyte, wherein the operator risks severe burns if the electrolyte should spill or splash, the necessity to expose the anode to the corrosive attack of the electrolyte during each startup and shutdown, and the necessity for difficult and exacting

¹² W. Juda et al., Abstract No. 353 in *Extended Abstracts*, The Electrochemical Society, Inc., New York, N.Y., 134th National Meeting, 1968. (See also R. L. Novack, D. M. Moulton, and W. Juda, French Patent 1,497,014 (6 October 1967).)

sealing procedures to prevent creepage and loss of electrolyte make frequent startup and shutdown of the cell impossible.

During operation, the cell is exacting in its demands as well. In order to prevent the hydroxide electrolyte from turning into carbonate, the air feed must be CO_2 -free. The fuel supply must be continuous and neither so great as to cause nickel precipitation on the electrolyte side of the anode or coking inside the anode in the reforming space nor so low as to allow corrosive attack of the electrolyte upon the membrane. The air supply must be continuous and be properly adjusted for the fuel-feed rate. The water supply must be continuous and be closely adjusted for the proper $\text{H}_2\text{O}:\text{C}$ ratio. The temperature must remain not only high enough to prevent failure of the anode by the phase-change mechanism, but also, it appears, high enough to allow the aluminum gasket to soften and thus prevent leakage of the electrolyte. Yet, too high a temperature will accelerate destructive corrosion of not only the palladium foil but also all parts of the cell exposed to the electrolyte.

Other apparent long-term problems are (1) settling of the catalyst in the anode causing bulging of the foil, which increases the possibility of shorting and also opens a possibility of fuel bypassing the reforming catalyst and (2) blockage of the air-inlet tubes by oxide deposits, requiring some provision for removing such deposits.^{13 14}

With all these factors requiring close control, the only likely possibility of a practical application would be a long-term, very constant use so that all parameters could be set once and then left constant, with changes or adjustments required only infrequently. Such prolonged use was achieved under the constant, closely controlled conditions at Prototech.

¹³ H. G. Petrow, Prototech, Inc., Private Communication.

¹⁴ R. L. Novack, U.S. Patent No. 3,471,333 (October 7, 1969).

APPENDIX A

LIQUID HYDROCARBON FEED SYSTEM FOR FUEL CELLS

The design and operation of a liquid hydrocarbon feed system for a reforming-anode fuel cell is described herein. This system will charge liquids at a smooth, steady rate of approximately 1 ml/h, but this rate may be varied by ± 50 percent. Figure A-1 shows the construction of the apparatus. Two identical buret-pressure systems feed alternately into a single feedline leading to the fuel cell so that one buret can be refilled while the other is feeding.

To prepare the system for operation, a pressure bulb is filled approximately two-thirds full of an 80-percent glycerine-20-percent water mixture containing sufficient dissolved copper sulfate to impart color to the solution. Gas pressure is applied to the pressure bulb, and the glycerine-water solution is forced first through the capillary and then through the bypass stopcock into the buret until the buret is nearly filled with solution. Liquid hydrocarbon is placed in the feed reservoir, and the three-way stopcock at the top of the buret is opened so that the reservoir is connected to the buret. The pressure is then removed from the bulb, and the capillary bypass stopcock is opened so that the glycerine-water solution runs back into the bulb, drawing hydrocarbon into the buret. The flow of solution is stopped before the solution reaches the bottom of the buret. Gas pressure is again applied to the bulb, the bypass is opened slightly, and the glycerine-water solution again is forced into the buret, raising the hydrocarbon in the buret and expelling air into the feed reservoir. These operations may be repeated if necessary to fill the buret completely with glycerine-water solution and with hydrocarbon with no air bubbles remaining. The final position of the glycerine-water-hydrocarbon interface should be within the graduated zone near the bottom of the buret. The other buret is filled in the same manner.

To feed the hydrocarbon to the fuel cell system, the three-way stopcock on the buret is turned so that the liquid is directed to the feed line, the capillary bypass is closed, and the pressure on the bulb is adjusted to the value required to give the desired rate. Consult the calibration curve (Figure A-2) for the capillary in use. These curves are only approximate, and direct calibration of each coil should be made after the unit is set up.

When the glycerine-water solution has risen in the feed buret to some point close to the zero graduation, the charging function is transferred to the standby system by turning the buret selector stopcock. The charge buret then may be refilled following

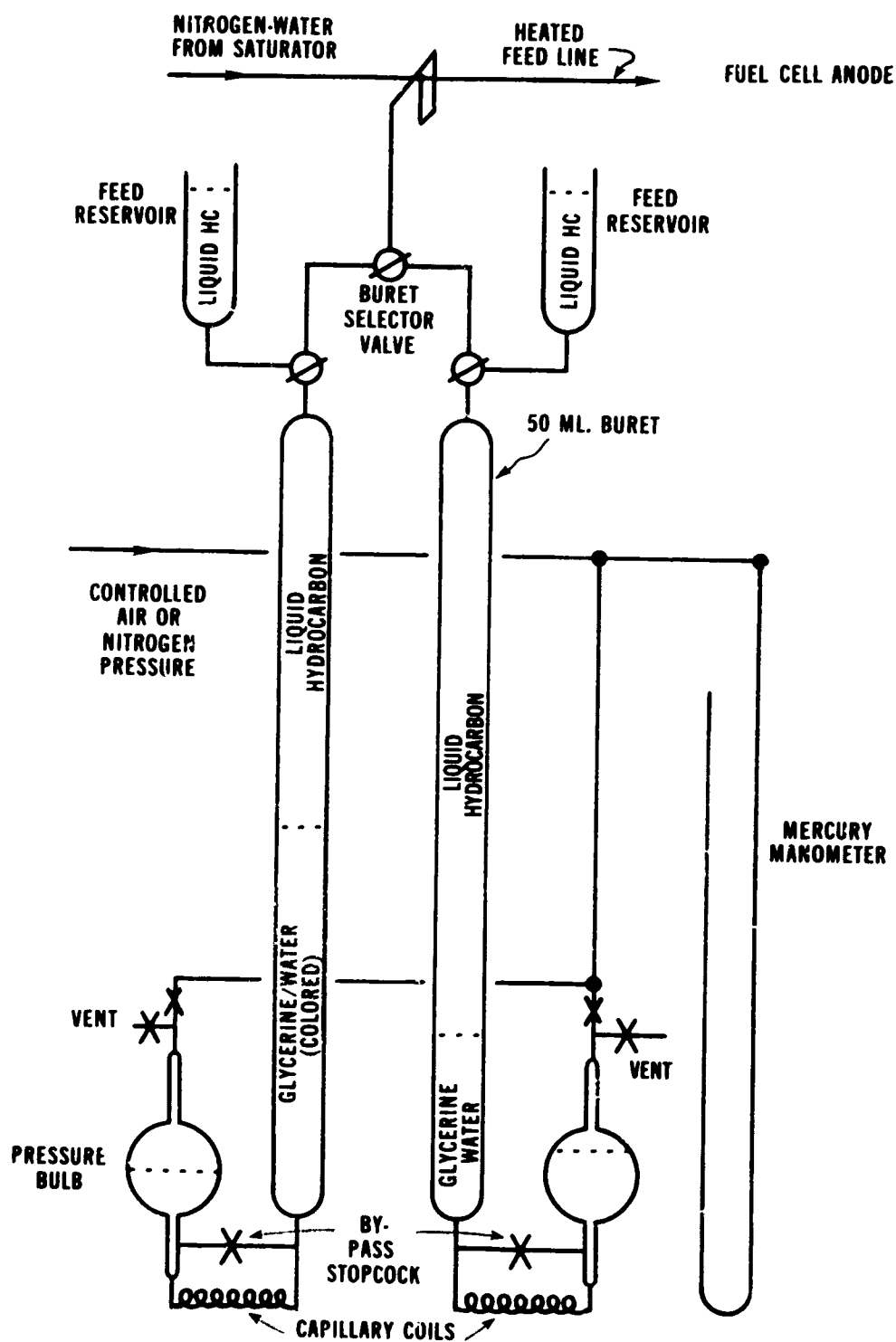


Figure A-1. Liquid hydrocarbon feed system.

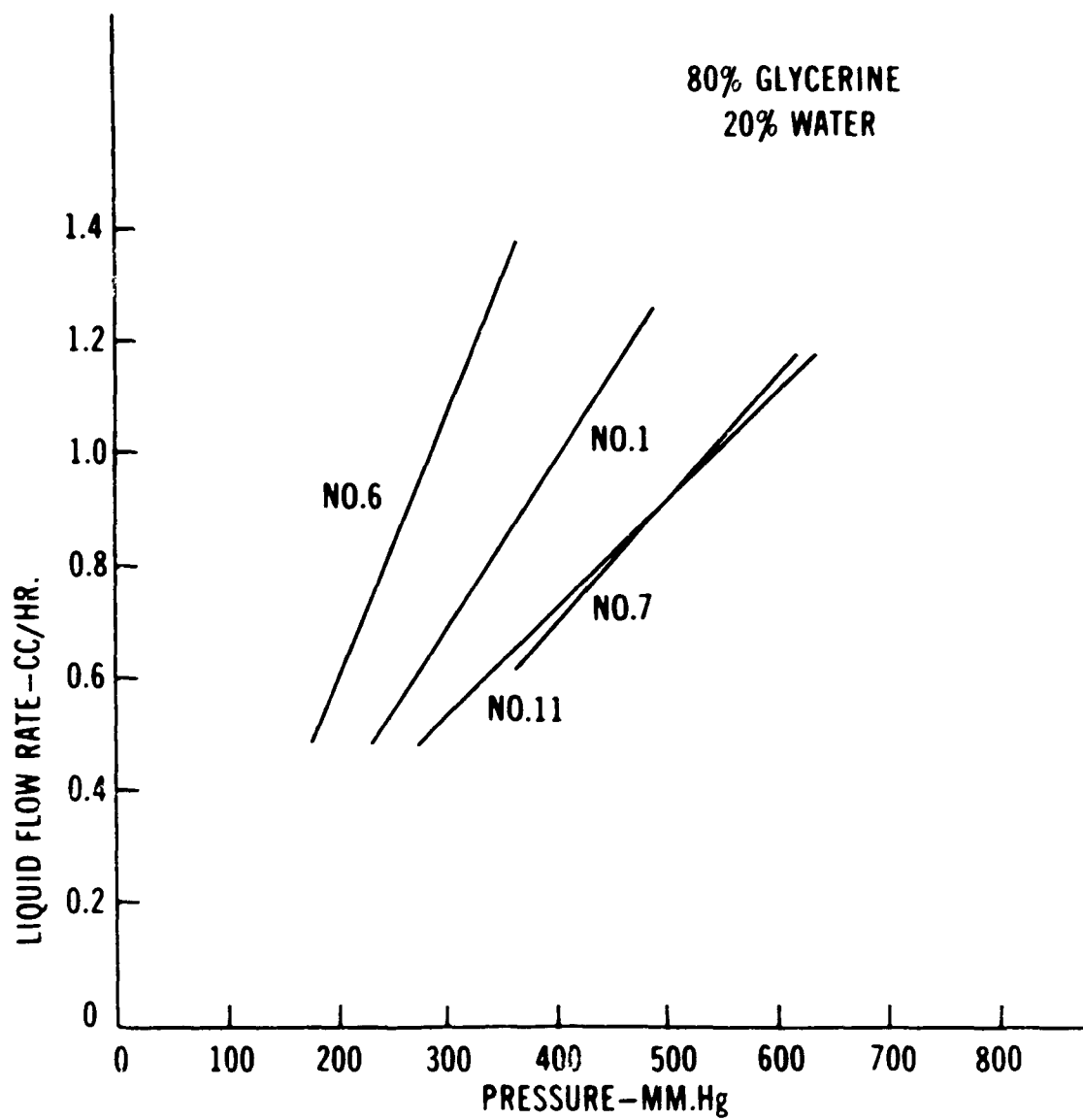


Figure A-2. Approximate calibration curves for liquid-feed capillaries.

the procedure used for the initial filling.

Several precautions must be observed in the operation of this system. Since the capillaries are of very small bore and plug easily, foreign solid matter must be carefully excluded. Care also must be taken to prevent the hydrocarbon from entering the capillary. To insure a constant feed rate, the gas pressure must be controlled fairly closely by a suitable pressure-control valve.

The heated feed line is a critical area of the system. A sufficient temperature must be maintained so that no condensation of the steam in the nitrogen-steam mixture from the saturator occurs. Even a slight amount of liquid water in the feed line will produce erratic cell operation and eventual coking of the catalyst. The ends of the feed line, at the Doty joints, are especially vulnerable to heat losses and condensation. On the other hand, the heat at the T-section where the hydrocarbon enters should not be great enough to cause vaporization of the feed more than a few millimeters back from the entrance point. It may be necessary to remove additional insulation from the tube at this point. Ideally, the hydrocarbon should vaporize completely just as it enters the horizontal feed line.

The feed tube was designed to meet two requirements. First, it is desirable to feed upward into the vaporization zone rather than downward so that gas bubbles do not become trapped in the feed line and cause erratic flows. Second, the leg extending down from the vaporization zone must be kept short to prevent settling of the heavy and less volatile components of the mixed hydrocarbon feed down into the buret. Also, capillary tubing is used to reduce component separation in the vaporization leg.

When the heater on the feed tube is operated at approximately 3 amperes, it gives sufficient heat to vaporize smoothly and completely the hydrocarbon at a rate of 1 ml/h and to maintain as steam the equivalent quantity of water. If a rate substantially greater than this is used, more current may be required, but it should not exceed about 5 amperes.

The capillary coils were designed for use with fuel cells operating in the 4- to 11-ampere range. One ml/h of UDEX raffinate is equivalent to 8.09 amperes at 100 percent fuel-utilization efficiency. If higher fuel cell currents are to be used, a higher hydrocarbon rate will be required; hence, larger capillaries must be used to prevent excessive pressures on the bulbs. The use of higher feed rates, however, presents fewer problems and gives smoother operation than low rates.

APPENDIX B

UDEX RAFFINATE

Drum 36-422

Analysis of Fuel Used in Tests

MS #9 6-2007

Component	Percent By:	
	Volume	Weight
n-Pentane	0.3	0.3
Paraffins		
C ₆	41.6	39.3
C ₇	31.0	30.4
C ₈	9.7	9.7
C ₉	1.4	1.5
MCP	8.9	9.8
DMCP	0.4	0.5
Alkylbenzenes		
C ₆	0.3	0.4
C ₇	2.0	2.5
C ₈	4.0	5.1
C ₉	0.3	0.4
Indans	0.1	0.1
	<u>100.0</u>	<u>100.0</u>
Paraffin C No.		6.6
Benzene C No.		7.7
Octane		60.5
d = 0.691 g/cm ³ @ Room Temperature		

UDEX Raffinate Test

Description – Liquid Hydrocarbon

Empirical Formula $C_{6.6} H_{14.5} \cong CH_{2.2}$

81.2% Paraffins (Mostly Branched)

10.3% Napthenes

8.5% Aromatics

<1 PPM Sulfur

Run Conditions: 455° C

90.10 Weight Ratio KOH: NaOH

35.3 CM² Anode Palladium Area

H₂O:C Ratio 2.3 - 3.5